Journal of Membrane Science 489 (2015) 28–35

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Chlorination of polyvinyl pyrrolidone–polysulfone membranes: Organic compound release, byproduct formation, and changes in membrane properties

Pengchao Xie [a,b], Charles-François de Lannoy [b,c], Jun Ma [a,*], Mark R. Wiesner [b,d,**]

[a] State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China
[b] Center for the Environmental Implications of Nanotechnology (CEINT), Durham 27708-0287, USA
[c] School of Earth Sciences, Stanford University, CA 94305, USA
[d] Department of Civil & Environmental Engineering, Duke University, Durham 27708-0287, USA

ARTICLE INFO

Article history:
Received 7 November 2014
Received in revised form
9 March 2015
Accepted 13 March 2015
Available online 30 March 2015

Keywords:
Chlorine
Polyvinyl pyrrolidone–Polysulfone
(PVP–PSF) membrane
Total organic carbon (TOC)
Byproducts

ABSTRACT

In this work, the release of organic compounds, the variations of membrane properties and the formation of toxic byproducts during chlorine treatment of polyvinyl pyrrolidone–polysulfone (PVP–PSF) membranes were investigated. Chlorine treatment decreased bovine serum albumin rejection, permeability and hydrophilicity of PVP–PSF membranes and resulted in the release of organic compounds as measured by total organic carbon (TOC). More organic compounds were released from the membranes at higher chlorine concentrations and higher initial values of chlorine contact pH. The presence of bromide that can be oxidized to bromine by chlorine also increased the release of organic matter from the membranes and contributed to the formation of high toxic brominated byproducts. Five toxic volatile chlorinated byproducts, chloroform, chloral hydrate, 1,1-dichloro-2-propanone, 1,1,1-trichloro-2-propanone and trichloronitromethane, were formed during chlorination of the organic compounds from the PVP–PSF membranes. Three brominated byproducts including bromodichloromethane, dibromochloromethane and bromoform were determined in the presence of bromide. The PVP appears to be more susceptible than PSF to chlorine destruction in the PVP–PSF membranes as analysis of the chlorinated byproducts derived from PVP precursors.

1. Introduction

The polysulfone (PSF) membrane is one of the most popular polymer membranes and is widely used in water treatment, wastewater reuse and desalination [1–3]. However, the hydrophobicity of the PSF membrane tends to favor organic fouling and biofouling [4,5]. Modification of PSF membrane to improve its properties including hydrophilicity, permeability, anti-fouling ability and tensile strength has been well developed [6–8]. Polyvinyl pyrrolidone (PVP) has been widely used as an additive when preparing PSF membranes due to its ability to increase membrane hydrophilicity and enlarge the macrovoids of PSF membrane, thereby increasing permeability [6,9]. The good miscibility of PVP with PSF and high solubility in water or a non-solvent facilitate modification of PSF membranes with PVP through simply mixing PVP in the casting solution for PSF membrane [10–12].

Chlorine is widely used as an oxidant or disinfectant in water treatment because of its low cost and high effectiveness [13]. Chlorine disinfection of feed water to membrane separation units is effective in managing biofilm growth on the membranes and associated membrane biofouling [14]. Prechlorination with 0.5–5 mg/L chlorine can also enhance the removal of metal ions and organic matter to control the inorganic and organic fouling [15–17]. Chlorine, at concentrations ranging from several mg/L to several hundred mg/L, is popular in cleaning fouled membranes and restoring the membrane flux [18]. The application of chlorine to manage biofouling of polymer membranes is usually performed following two operational modes at water treatment facilities [18,19]. First, the addition of chlorine may be performed to prevent the biofouling by back-flushing with water containing 2–8 mg/L NaOCl every 15–60 min [19,20]. Also, fouled membranes may be cleaned by soaking them in 20–400 mg/L chlorine solution at a frequency of once a day to every several weeks [19,20]. It is therefore important to evaluate the effect of chlorine on the

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[*] Corresponding author. Tel.: +86 451 86282292; fax: +86 451 86283010.

[**] Corresponding author at: Center for the Environmental Implications of Nanotechnology (CEINT), Durham 27708-0287, USA. Tel.: +1 919 660 5292; fax: +1 919 660 5219.

E-mail addresses: majun@hit.edu.cn (J. Ma), wiesner@duke.edu (M.R. Wiesner).

http://dx.doi.org/10.1016/j.memsci.2015.03.058
0376-7388/

performance and lifetime of polymer membranes. For example, chemical cleaning of polyethersulfone membrane by hypochlorite at high concentrations significantly impaired the membrane properties including mechanical strength, integrity and electronegativity [19]. Polyamide membranes are well-known to be highly vulnerable to chlorine attack [21–24]. Organic compounds containing pyrrole rings are also susceptible to be attacked by chlorine [25,26]. While chlorine is generally considered to be relatively compatible with PSF-derived membranes, there is little information related to the potential impact of chlorine oxidation, especially at low dosage, on PVP–PSF membranes concerning the formed byproducts. Chlorine reacts with organic matter to produce toxic chlorinated byproducts through addition or electrophilic substitution [13]. The common precursors of the toxic chlorinated byproducts include natural organic matter, algal organic matter and bacterial [27–30]. It is unknown whether or not the organics present in PVP–PSF membranes may serve as the precursors of chlorinated byproducts during chlorine cleaning membrane. Thus, the goal of the current study is to evaluate the damage of PVP–PSF membranes and the formation of selected byproducts when chlorine is brought into contact with PVP–PSF membranes.

We selected prepared PVP–PSF membranes for this study as they are widely used in drinking water treatment and wastewater reuse [1,2]. The release of organic matter from these membranes, the variations of the membrane properties, and the formation of some volatile chlorinated byproducts were evaluated when membranes were exposed to chlorine under controlled conditions. The impact of membrane thickness and several operation processes including pre-soaking time, chlorine dosage and initial pH were evaluated. The role of bromide was also examined as bromide is always detected in source water, filtered water and tap water and may react with chlorine to form bromine [31].

2. Experimental section

2.1. Chemicals

All chemicals of reagent-grade were obtained from commercial sources and used as received without further purification. All the stock solutions were prepared in ultra pure water (18.2 MΩ cm) produced from a Nanopure system (Barnstead). Polyvinyl pyrrolidone (PVP, 40 kDa), polysulfone (PSF, 35 kDa), cellulose acetate (CA, 30 kDa), potassium bromide ($\geq 99\%$) and bovine serum albumin (BSA, $\geq 98\%$) were purchased from Sigma-Aldrich, USA. Dimethyl formamide (DMF, 36,000 Da), methyl tert-butyl ether (HPLC grade) and sodium nitrite ($\geq 97\%$) were obtained from Fisher, USA. A free chlorine stock solution (3200 mg/L as Cl_2) was prepared from a 6% sodium hypochlorite solution (NaOCl, VWR International) and standardized periodically by DPD ferrous titrimetric method [32]. The pH of solution was adjusted by sodium hydroxide ($\geq 97\%$, VWR International, USA) and sulfuric acid (96%, Acros Organics, USA). Standard kits for measuring trihalomethanes (THMs), haloketones (HKs), haloaldehydes (HAs), haloacetonitriles (HANs), trichloronitromethane (TCNM) and trichloroacetamide (TCAcAm) were obtained from Sigma-Aldrich. A standard of dichloroacetamide (DCAcAm) was bought from Alfa Aesar, USA.

2.2. Membrane preparation

PVP–PSF membranes were prepared based on the procedures described previously [33]. Polymer solutions for fabricating the PVP–PSF membranes were prepared in DMF containing 17 wt% PSF and 6 wt% PVP. The polymer mixture was heated to 60 °C and stirred continuously until the PVP and PSF were fully dissolved and the mixture was homogeneous. Then the polymer solution was cast with a casting knife set on a glass plate. The glass plate with casting solution was transferred into a basin filled with fresh DI water, in which the membrane precipitated and released from the glass plate. After remaining in the water bath for 20 min, the membrane was transferred into fresh DI water and stored at 4 °C for 7 days (except in cases where the impact of pre-soaking time was evaluated). The DI water was changed every day (24 h) in order to ensure the removal of residual DMF. The resulting membranes (without glycerin treatment) were then air-dried at room temperature for subsequent use based on the discussion shown in Text S1.

Polymer solutions for making PSF and CA membranes (used to evaluate the role of PVP) were prepared in DMF containing 17 wt% PSF and 17 wt% CA, respectively. The other operating procedures were the same as those described for preparing PVP–PSF membranes.

2.3. Experimental procedure

Oxidation experiments were carried out at room temperature (25 °C) with 200 mL DI water in triangular flasks under stirring with a magnetic stirrer. When determining the impact of bromide, $0-10$ μM potassium bromide was added in the DI water. Hypochlorite of the desired concentration ($0-14.2$ mg/L as Cl_2) and a piece of circular membrane with a radius of 2.5 cm were added to the solution. The initial contact pH was adjusted to 8.5 for all the samples except when evaluating the impact of initial pH ($4.3-9.0$). Samples were withdrawn at predetermined time intervals and quenched by adding excess sodium nitrite before analysis. After oxidation for 60 min, the solutions were collected and stored in amber glass bottles capped with Teflon-faced septa to determine the formation potential of toxic volatile chlorinated byproducts. The samples were incubated at room temperature in the dark for 3 days and then quenched by adding excess ascorbic acid for the chlorinated byproduct analyses. All the experiments were replicated at least twice, and the error bars shown in all the figures represent the standard deviation from the replicated tests.

2.4. Analytical method

A TOC analyzer (TOC-L, Shimadzu, Japan) was used to determine the concentration of TOC. The concentration of residual chlorine was measured by DPD ferrous titrimetric method [32]. The hydrophilicity was determined by measuring contact angle (Easy Drop, Kruss GmbH, German). More than 10 contact angles at different places of each membrane were recorded, then an average value of the remaining angles after discarding the lowest and highest values was calculated. Measurements of permeability were carried out with DI water at different pressures ranging from 172 kPa to 690 kPa (25 psi to 100 psi) by using a steel pressure dead-end cell (Sterlitech, USA). BSA rejection was measured by feeding 0.1% BSA solution to a piece of membrane at a constant pressure of 690 kPa. A UV–vis spectrometer (Cary 100, Agilent Technologies, USA) was used to measure the concentration of BSA by recording the absorbance at a wavelength of 278 nm. A gas chromatography (GC 2014, Shimadzu, Japan) coupled with an electron capture detector (ECD) and a DB-624 column (30 m × 0.32 mm, ID × 1.8 μm) was employed to measure halogenated byproducts based on U.S. Environmental Protection Agency method 551.1 [34]. The temperatures of the injector and ECD were 170 °C and 290 °C, respectively. The temperature program of the oven began at 35 °C for 9 min, ramped to 40 °C at 2 °C/min and held for 8 min, ramped to 80 °C at 20 °C/min, ramped to 160 °C at 40 °C/min and held for 4 min, and then ramped to 200 °C at 40 °C/min and held for 5 min.